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(54) OPTICAL GLASS

(57)Abstract:

PURPOSE: To obtain an optical glass having a good chemical resistance while maintaining prescribed optical constants and a yield point suitable for a mold press process, by using SiO₂, B₂O₃, SrO and Li₂O as essential components and specifying the other components to limit compositions of the components.

CONSTITUTION: An optical glass contains components in ranges of composition in wt.% as SiO₂: 25-50%, B₂O₃: 16-40%, Al₂O₃: 0-5%, TiO₂: 0-1%, ZrO₂: 0-5%, ZnO: 0-5%, MgO: 0-5%, CaO: 0-8%, SrO: 5-25%, BaO: 0-9%, Li₂O: 1-10%, Na₂O+ K₂O: 0-5% and Sb₂O₃: 0-1%, and also has optical constants within certain ranges such as a refractive index (N_d) of 1.55-1.65, and an Abbe number (ν_d) of 55-63. Also to improve melting property and devitrification resistance of the glass, the other components than shown above, e.g. La₂O₃, Bi₂O₃, Cs₂O, SnO, F, etc., may be added, as necessary.

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CLAIMS

(57) [Claim(s)]

[Claim 1] At weight %, it is SiO₂ 25 - 50%, B₂O₃ 16 - 40%, aluminum 2O₃ 0 - 5%, TiO₂ 0 - 1%, ZrO₂ 0 - 5%, Less than 0 - 5% of ZnO(s), MgO 0 - 5%, CaO 0 - 8%, SrO 11 - 25%, BaO 0 - 6%, Li₂O 1 - 10%, Na₂O+K₂O 0 - 5%, and Sb 2O₃ It consists of each component of 0 - 1% of range. Optical glass characterized by for a refractive index (Nd) having 1.55 to less than 1.63, and the Abbe number (nud) having the optical constant of the range of 59-63.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to less than [refractive-index (Nd) 1.55-1.63] and the optical constant of the range of the Abbe numbers (nud) 59-63, and the optical glass of the $\text{SiO}_2\text{-B-2O}_3\text{-SrO-Li}_2\text{O}$ system which has the outstanding chemical durability to an acid, i.e., acid resistance, and a low-temperature softening degree.

[0002]

[Description of the Prior Art] From the former, the heavy crown system glass which has the aforementioned optical constant is known variously, for example, much SK (shot catalog name) type glass is indicated in "a glass composition data book and 1991 (Glass Manufacturers' Association of Japan issue)." However, these glass is unsuitable as glass for a mould press for fabricating directly the optical element to which molding temperature does not need grinding or polish after press forming by becoming high, in order that a surrendering point (At) may generally exceed 600 degrees C highly. Since problems, such as the endurance of mold material, will arise if molding temperature becomes an elevated temperature in a mould press, the surrendering point of glass has an as much as possible desirable method of a low. In order to solve these problems, the glass of the system which introduced R'2O (R' is alkali metal) is proposed [*****]. For example, although what made TeO_2 component indispensable is indicated by JP.4-292435,A since chemical durability becomes bad when R'2O is only introduced into composition of the conventional $\text{SiO}_2\text{-B-2O}_3\text{-BaO}$ system, this glass has bad acid resistance. Moreover, since acid resistance tends to produce YAKE on a glass front face bad like the above, the thing of the $\text{SiO}_2\text{-B-2O}_3\text{-CaO-Li}_2\text{O}$ system currently indicated by JP.60-122747,A is unsuitable as glass for a mould press.

[0003]

[Problem(s) to be Solved by the Invention] this invention aims at offering the optical glass which has the outstanding chemical durability to an acid, maintaining the surrendering point (At) of having been suitable for less than [refractive-index (Nd) 1.55-1.63], and the optical constant and mould press of the range of the Abbe numbers (nud) 59-63.

[0004]

[Means for Solving the Problem] the optical glass which this invention person has the aforementioned predetermined optical constant in the $\text{SiO}_2\text{-B-2O}_3\text{-SrO-Li}_2\text{O}$ system glass of the specific range which is not specifically indicated by the Prior art as a result of it repeated test research wholeheartedly in order it attains the above-mentioned purpose, and has the low-temperature softening degree suitable for a mould press, i.e., the outstanding chemical durability to the point surrendering [low] and an acid, is obtained -- **** -- it came make a broth and this invention

[0005] The feature of the optical glass concerning this invention is weight %, and is SiO_2 25 - 50%, B-2 O₃ 16 - 40%, aluminum 2O₃ 0 - 5%, TiO₂ 0 - 1%, 2O - 5% of ZrO(s), ZnO Less than 0 - 5%, MgO 0 - 5%, CaO 0 - 8%, SrO 11 - 25%, BaO 0 - 6%, Li₂O 1 - 10%, Na₂O+K₂O 0 - 5%, and Sb 2O₃ It is in the place which consists of each component of 0 - 1% of range, and has less than [refractive-index (Nd) 1.55-1.63] and the optical constant of the range of the Abbe numbers (nud) 59-63.

[0006] The reason which limited the composition range of each component is as above-mentioned as follows. When the chemical durability of glass falls that the amount is less than 25% and the amount exceeds 50%, while it becomes impossible for a low-temperature softening degree to maintain SiO_2 component, it becomes impossible that is, to maintain the optical constant made into the target of this invention. Although B-2O₃ component is a component effective in giving a low-temperature softening degree to glass, if devitrification-proof nature gets worse at less than 16% and the amount exceeds 40%, chemical durability will get worse. 2Aluminum₃ component is effective in improvement in the chemical durability of glass. However, elevation of submission temperature (At) is imitated at the same time devitrification-proof nature will get worse, if the amount exceeds 5%, and it is **.

[0007] Although TiO₂ component can be added because of solar RIZESON prevention of glass and optical constant adjustment, 1% or less is enough as the amount. Although ZrO₂ component can be added if needed since it raises a refractive index and improves chemical durability, if it exceeds 5%, devitrification-proof nature will get worse. [0008] a SrO component shows the outstanding acid resistance, maintaining a low-temperature softening degree by coexisting with B-2O₃ component of the specific range in this invention -- **** -- it is the important component which took out it is the conventional glass composition system which has the aforementioned optical constant, and although the SrO component was used for adjustment of an optical constant etc. as a component which shows the same property as BaO and CaO, SrO components are low dispersibility and chemical durability, and a still more advantageous synthetic component in respect of a low-temperature softening degree compared with other divalent metal oxide components in raising the refractive index of glass by this composition system -- **** -- it took out A lot of introduction was conventionally difficult for the SrO component in order to worsen the stability of glass. However, very stable glass was able to be obtained by making the B-2O₃ aforementioned component 16% or more. In order to obtain the chemical durability and the low-temperature softening degree which were excellent as above-mentioned, maintaining the stability of glass, acid resistance becomes 11 - 25% of the amount is effective, and inadequate at less than 11%, and if it exceeds 25%, glass will become unstable on the contrary. Although it can add because of optical constant adjustment etc., while the stability of glass becomes is it easy to be spoiled that the amount of a ZnO component is 5% or more as for ZnO, MgO, CaO, and the BaO component which are other divalent metal oxide components, chemical durability gets worse. Moreover, if the amount of MgO, CaO, and a BaO component exceeds 5%, 8%, and 6%, respectively, while the stability of glass will become is easy to be spoiled, chemical durability gets worse.

[0009] since especially the effect of giving a low-temperature softening property to glass is large, a Li₂O component is an

important component — in order to demonstrate the effect, maintaining the devitrification-proof nature of glass, you should make the amount 1 - 10% of range. Although a Na₂O and K₂O component may be made to add if needed in order to acquire a low-temperature softening property, the amount should carry out those total quantities to 5% or less for devitrification-proof nature and chemical durability maintenance. Although 2OSb₃ component can be arbitrarily added as a clarifier in the case of glass melting, less than 1% is enough as the amount.

[0010] [Example] Next, it was shown in Table 1 with the refractive index (Nd) of the glass obtained, respectively about the example of operation composition concerning the optical glass of this invention (No.1-No.5), and the example of comparison composition of the aforementioned conventional optical glass (No.A-No.C), the Abbe number (nud), the surrendering point (At, **), and the measurement test result of chemical durability.

[0011] The acid-proof sex test is immersed for 30 minutes into 3N-nitric-acid solution (25 degrees C) in each glass sample (about 30x30x5mm) which has the fracture surface and a polished surface. that by which the erosion degree of both front faces is observed, it is changeless also on the surface of any, and transparency was maintained — O mark — displaying — moreover, both front faces — all adopted the method of displaying that by which the dry area was produced and transparency was spoiled by whether it is Ming by x mark. In addition, after these glass samples carry out weighing capacity mixture of the usual raw materials for optics, such as an oxide, a carbonate, a nitrate, and a hydroxide, at a predetermined rate, they are supplied to a platinum crucible, and after fusing for about 2 to 4 hours and carrying out stirring homogenization at the temperature of 1150-1350 degrees C according to the difficulty of melting by composition, they can be easily obtained by casting and cooling slowly to metal mold etc.

[0012]

[Table 1]

単位 ; 重量%

No.	実施例					比較例		
	1	2	3	4	5	A	B	C
SiO ₂	27.4	42.0	44.0	46.8	50.0	38.7	42.0	45.8
B ₂ O ₃	40.0	24.0	23.0	19.6	16.0	14.9	24.0	12.0
Al ₂ O ₃		1.0	3.0			5.0	1.0	4.0
TiO ₂	1.0		0.2		0.1			
ZrO ₂			1.0					
ZnO	4.6	3.0	1.6		1.8			8.0
CaO	7.0		3.0		3.0			20.0
SrO	11.0	22.8	17.1	24.5	20.6			
BaO	2.0					40.1	22.8	
Li ₂ O	6.0	7.0	7.0	9.0	8.0		7.0	5.0
Na ₂ O								5.0
Sb ₂ O ₃	1.0	0.2	0.1	0.1	0.5	1.0	0.2	0.2
As ₂ O ₃						0.3		
TeO ₂							3.0	
n d	1.5944	1.5834	1.5792	1.5868	1.5886	1.5891	1.5818	1.5910
v d	59.7	62.7	61.8	62.9	61.7	61.3	62.8	57.0
A t	537	541	549	532	533	650	540	549
耐酸性	○	○	○	○	○	○	×	×

[0013] Each glass of the example of this invention has a predetermined optical constant and the predetermined point (At) surrendering [low], and, moreover, improves much more rather than the conventionally well-known, acid resistance, i.e., the chemical durability to an acid, example glass of comparison as it sees in Table 1. Moreover, each of these glass is excellent in devitrification-proof nature, and it is easy to homogenize it. For this reason, the glass of the above-mentioned example is easy to manufacture, and suitable as a material for a mould press.

[0014]

[Effect of the Invention] Since the optical glass of this invention has specific composition of a SiO₂-B₂O₃-SrO-Li₂O system, it has less than [refractive-index (Nd) 1.55-1.63], and the optical constant and the point (At) surrendering [low] of the range of the Abbe numbers (nud) 59-63, and the chemical durability to an acid is excellent much more compared with conventional glass, as stated above. Moreover, manufacture is easy, and it is easy to homogenize, and is suitable for the mould press.

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(56) 参考文献 特開 昭54-3115 (J P, A)

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(54) 【発明の名称】 光学ガラス

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(57) 【特許請求の範囲】

【請求項1】 重量%で、 SiO_2 25~50%、 B_2O_3 16~40%、 Al_2O_3 0~5%、 TiO_2 0~1%、 ZrO_2 0~5%、 ZnO 0~5%未満、 MgO 0~5%、 CaO 0~8%、 SrO 1~25%、 BaO 0~6%、 Li_2O 1~10%、 $\text{Na}_2\text{O} + \text{K}_2\text{O}$ 0~5%および Sb_2O_3 0~1%の範囲の各成分からなり、屈折率(Nd)が1.55~1.63未満、アッペ数(ν_d)が59~63の範囲の光学恒数を有することを特徴とする光学ガラス。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は、屈折率(Nd) 1.55~1.63未満及びアッペ数(ν_d) 59~63の範囲の光学恒数と、酸に対する優れた化学的耐久性、すな

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わち、耐酸性及び低温軟化性を有する $\text{SiO}_2 - \text{B}_2\text{O}_3 - \text{SrO} - \text{Li}_2\text{O}$ 系の光学ガラスに関する。

【0002】

【従来の技術】 従来から、前記の光学恒数を有する重ク라운系ガラスが種々知られており、例えば「ガラス組成データブック・1991年((社) 日本硝子製品工業会発行)」には、SK(ショットカタログ名称)タイプのガラスが多数記載されている。しかし、これらのガラスは、一般に屈伏点(At)が高く600℃を超えるため成形温度が高くなり、プレス成形後に研削または研磨を必要としない光学素子を直接成形するためのモールドプレス用ガラスとしては不適當である。モールドプレスにおいて成形温度が高温になると型材の耐久性等の問題が生じるため、ガラスの屈伏点は可能なかぎり低い方が望ましい。これらの問題を解決するためとして、R' 2

〇(R'はアルカリ金属)を導入した系のガラスが提案されている。例えば特開平4-292435号公報には、従来の SiO_2 - B_2O_3 - BaO 系の組成にR'の O を単に導入した場合、化学的耐久性が悪くなるため、 TeO_2 成分を必須としたものが開示されているが、このガラスは耐酸性が悪い。また特開昭60-122747号に開示されている SiO_2 - B_2O_3 - CaO - Li_2O 系のもは、上記と同様に耐酸性が悪くガラス表面にヤケを生じやすいため、モールドプレス用のガラスとしては不相当である。

【0003】

【発明が解決しようとする課題】本発明は、屈折率(Nd)1.55~1.63未満及びアッペ数(νd)5.9~6.3の範囲の光学恒数とモールドプレスに適した屈伏点(At)を維持しつつ、酸に対する優れた化学的耐久性を有する光学ガラスを提供することを目的とする。

【0004】

【課題を解決するための手段】上記目的を達成するため本発明者は、鋭意試験研究を重ねた結果、従来の技術には具体的には開示されていない特定範囲の SiO_2 - B_2O_3 - SrO - Li_2O 系ガラスにおいて、前記所定の光学恒数を有し、モールドプレスに適した低温軟化性、すなわち低い屈伏点と酸に対する優れた化学的耐久性を有する光学ガラスが得られることをみだし、本発明をなすに至った。

【0005】本発明にかかる光学ガラスの特徴は、重量%で、 SiO_2 25~50%、 B_2O_3 16~40%、 Al_2O_3 0~5%、 TiO_2 0~1%、 ZrO_2 0~5%、 ZnO 0~5%未満、 MgO 0~5%、 CaO 0~8%、 SrO 11~25%、 BaO 0~6%、 Li_2O 1~10%、 $\text{Na}_2\text{O}+\text{K}_2\text{O}$ 0~5%および Sb_2O_3 0~1%の範囲の各成分からなり、かつ、屈折率(Nd)1.55~1.63未満、アッペ数(νd)5.9~6.3の範囲の光学恒数を有するところにある。

【0006】上記のとおり、各成分の組成範囲を限定した理由は次のとおりである。すなわち SiO_2 成分は、その量が25%未満であるとガラスの化学的耐久性が低下し、またその量が50%を超えると低温軟化性が維持できなくなるとともに、本発明の目標とする光学恒数を維持できなくなる。 B_2O_3 成分はガラスに低温軟化性を与えるのに有効な成分であるが、その量が16%未満では耐失透性が悪化し、40%を超えると化学的耐久性が悪化する。 Al_2O_3 成分は、ガラスの化学的耐久性の向上に有効である。しかし、その量が5%を超えると耐失透性が悪化すると同時に屈伏温度(At)の上昇をまねく。

【0007】 TiO_2 成分は、ガラスのソーラリゼーション防止と光学恒数調整のため添加し得るが、その量は1%以下で十分である。 ZrO_2 成分は、屈折率を高め

化学的耐久性を改善するため必要に応じ添加し得るが、5%を超えると耐失透性が悪化する。

【0008】 SrO 成分は、本発明において特定範囲の B_2O_3 成分と共存することにより、低温軟化性を維持しつつ、優れた耐酸性を示すことをみだした重要な成分である。前記の光学恒数を有する従来のガラス組成系で、 SrO 成分は BaO 、 CaO と同じ性質を示す成分として光学恒数の調整等に用いられていたが、本組成系で SrO 成分はガラスの屈折率を高めるうえ、他の2価金属酸化物成分と比べ、低分散性及び化学的耐久性、さらに低温軟化性の点で総合的に最も有利な成分であることをみだしたのである。従来 SrO 成分はガラスの安定性を悪化させるため、多量の導入が困難であった。ところが前記の B_2O_3 成分を16%以上にすることで極めて安定なガラスを得ることができたのである。上記のとおり、ガラスの安定性を維持しつつ優れた化学的耐久性及び低温軟化性を得るためには、その量は11~25%が有効であり、11%未満では耐酸性が不十分となり、25%を超えるとかえってガラスが不安定になる。他の2価金属酸化物成分である ZnO 、 MgO 、 CaO 及び BaO 成分は、光学恒数調整等のため添加し得るが、 ZnO 成分の量が5%以上であるとガラスの安定性が損なわれやすくなると同時に化学的耐久性が悪化する。また、 MgO 、 CaO 及び BaO 成分の量が、それぞれ5%、8%及び6%を超えるとガラスの安定性が損なわれやすくなると同時に化学的耐久性が悪化する。

【0009】 Li_2O 成分は、ガラスに低温軟化特性を与える効果が特に大きいので重要な成分であるが、ガラスの耐失透性を維持しつつその効果を発揮させるためには、その量は1~10%の範囲にすべきである。 Na_2O 及び K_2O 成分は、低温軟化特性を得るために必要に応じ添加させ得るが、その量は耐失透性と化学的耐久性維持のため、それらの合計量を5%以下にすべきである。 Sb_2O_3 成分は、ガラス溶融の際の澄清剤として任意に添加し得るが、その量は1%以内で十分である。

【0010】

【実施例】次に、本発明の光学ガラスにかかる実施組成例(No. 1~No. 5)及び前記従来の光学ガラスの比較組成例(No. A~No. C)についてそれぞれ得られたガラスの屈折率(Nd)、アッペ数(νd)、屈伏点(At、°C)及び化学的耐久性の測定試験結果とともに表1に示した。

【0011】耐酸性試験は、破面及び研磨面を有する各ガラス試料(約30×30×5mm)を3N-硝酸水溶液(25°C)中に30分間浸漬して両表面の浸蝕度合を観察し、いずれの表面にも変化がなく透明性が維持されたものを○印で表示し、また両表面いずれも荒れを生じ透明性が明かに損なわれたものを×印で表示する方法を採用した。なお、これらのガラス試料は酸化物、炭酸塩、硝酸塩、水酸化物等の通常の光学用原料を所定の割

合で秤量混合した後白金坩堝に投入し、組成による溶融
の難易度に応じて1150～1350℃の温度で約2～
4時間溶融し、攪拌均質化した後、金型等に鑄込み徐冷*

*することにより容易に得ることができる。

【0012】

【表1】

単位；重量%

No.	実施例					比較例		
	1	2	3	4	5	A	B	C
SiO ₂	27.4	42.0	44.0	46.8	50.0	38.7	42.0	45.8
B ₂ O ₃	40.0	24.0	23.0	19.6	16.0	14.9	24.0	12.0
Al ₂ O ₃		1.0	3.0			5.0	1.0	4.0
TiO ₂	1.0		0.2		0.1			
ZrO ₂			1.0					
ZnO	4.6	3.0	1.6		1.8			8.0
CaO	7.0		3.0		3.0			20.0
SrO	11.0	22.8	17.1	24.5	20.6			
BaO	2.0					40.1	22.8	
Li ₂ O	6.0	7.0	7.0	9.0	8.0		7.0	5.0
Na ₂ O								5.0
Sb ₂ O ₃	1.0	0.2	0.1	0.1	0.5	1.0	0.2	0.2
As ₂ O ₃						0.3		
TeO ₂							3.0	
n _d	1.5944	1.5834	1.5792	1.5868	1.5886	1.5891	1.5818	1.5910
v _d	59.7	62.7	61.8	62.9	61.7	61.3	62.8	57.0
A _t	537	541	549	532	533	650	540	549
耐酸性	○	○	○	○	○	○	×	×

【0013】表1にみられるとおり、本発明の実施例のガラスはいずれも所定の光学恒数と低い屈伏点（A_t）とを有し、しかも耐酸性、すなわち、酸に対する化学的耐久性が従来公知の比較例ガラスよりも一段と改善されている。また、これらのガラスはいずれも耐失透性に優れ、また均質化しやすい。このため上記実施例のガラスは製造が容易であり、モールドプレス用素材として適している。

【0014】

【発明の効果】以上に述べたとおり、本発明の光学ガラスはSiO₂-B₂O₃-SrO-Li₂O系の特定組成を有するものであるから、屈折率（N_d）1.55～1.63未満、アッベ数（v_d）59～63の範囲の光学恒数と低い屈伏点（A_t）とを有し、かつ、従来のガラスに比べて酸に対する化学的耐久性が一段と優れている。また、製造が容易であり、均質化しやすく、モールドプレスに適している。